Supporting Information

Ji et al. 10.1073/pnas.1705463114

Experimental Method

The flow reactor was constructed from precision-bore Pyrex tubing of 2.0 cm i.d. and 75cm in length. All surfaces exposed to the radicals were coated with halocarbon wax to reduce wall loss. A flow of nitrogen carrier gas (~ 30 l min^{-1}) was introduced into the flow reactor through an entrance port in the sidearm of the flow reactor (Fig. S1). A high-capacity (700 L min^{-1}) oil-free dry scroll pump was used to evacuate the flow reactor through an exit port in the downstream end of the reactor and the majority of the flow was directed through this port. Only a small fraction (about 1%) of the flow was extracted into the drift tube through a small orifice (1 mm). The pressure in the flow reactor was monitored by a capacitance manometer (1000 Torr full scale) in the downstream end of the flow reactor and was regulated at about 100 Torr under the turbulent flow condition (S1). All experiments were performed at 298 ± 2 K. Typical flow velocity in the flow reactor ranged from 800 to 1500 cm s^{-1}. All the gas flows were monitored with calibrated mass flow meters (Millipore Tylan 260 Series). A quadropule mass detector was employed to filter and analyze the mass of the reactants, intermediates and products under the counting mode operation.

The hydroxyl radical OH was generated by the following reaction (S2),

$$H + NO_2 \rightarrow OH + NO \quad (1)$$

OH radicals were produced by introducing a small amount of 3% H_2/He mixture through a microware discharge followed by adding an excess of a 1% NO_2/He mixture downstream. OH radicals were detected using the negative reagent ion SF_6^-. A negative voltage (-5kv) was applied to the electrode of a corona discharge, by which the molecules of SF_6 were ionized. SF_6^- and OH^- were then guided by a weak negative electric field (about 2.0 Volt cm^{-1}) through the drift tube. The OH concentration was estimated using the procedures similar to those in our previous studies (S2).

The products from the OH-toluene reactions were monitored and quantified using hydronium ion (H_3O^+) as the reagent ion. H_3O^+ ions were generated by leaking a small amount of water vapor from a bubbler containing deionized water into the nitrogen flow, which then passed through the corona discharge. For the proton transfer reaction,

$$R + H_3O^+ \rightarrow H_2O + RH^+ \quad (2)$$

only a small fraction of reagent ions H_3O^+ were converted into product the ion RH^+, which was then detected by ID-CIMS. Calibration showed an excellent agreement between the toluene concentrations estimated from the known volumetric mixing ratio of the gas standard in the flow reactor and that measured by the ID-CIMS method (within 10%).

The experimental procedures for product measurements of the OH-initiated oxidation of toluene in the presence of O_2 and NO were similar to those in our previous studies (S1,S3). The unique feature of the flow reactor/ID-CIMS technique lies in its capability of quantifying the product yields without the necessity of calibration with authentic samples, as we have previously

demonstrated the application to quantify product yields from OH-isoprene and OH-m-xylene reactions (S1,S3). The product yield of the OH-toluene reactions is derived from,

$$Y\ (\%) = k_{tol}/k_{prod} \times \Delta S_{prod}/\Delta S_{tol} \quad (3)$$

where k_{prod} and k_{tol} are the ion-molecule rate constants of the product and toluene with H_3O^+, respectively. $\Delta S_{prod}/\Delta S_{tol}$ is the ratio of the protonated product formed to the protonated toluene consumed. The ion-molecule reaction constants were calculated from the ADO theory, which has been validated for accurate determination of the reaction rates between H_3O^+ and a series of hydrocarbons and oxygenated organic species (S1).

Commercially available toluene (Sigma-Aldrich, 99.5%) was used as received without further purification. The following gases were purchased from Matheson-Trigas: H_2 (99.999%), O_2 (99.98%), NO_2 (99.5%), SF_6 (99.996%) and from Aldrich Chemical: NO (98.5%). Deionized water (18MΩ·cm) was generated from Barnstead E-Pure Water System. Mixture of 0.5% toluene/He was prepared volumetrically in a 2 L glass bulb. The toluene mixture, along with a small carrier flow of N_2, was introduced into the flow reactor using a 10 sccm flow meter. NO was introduced through an activated carbon trap to remove impurities (e.g., NO_2) before being added to the reactor.

References

S1. Zhao J, Zhang R, Misawa K, Shibuya K (2005) Experimental product study of the OH-initiated oxidation of m-xylene. *J Photoch Photobio A* 176:199–207.

S2. Zhang D, Zhang R North SW (2003) Experimental study of NO reaction with isoprene hydroxyalkyl peroxy radicals. *J Phys Chem A* 107:11013–11019.

S3. Zhao J, Zhang R, Fortner EC, North SW, Quantification of hydroxycarbonyls from OH-isoprene reactions. *J Am Chem Soc* 126:2686–2687.

Table S1. Summary of the experimental conditions, i.e., the total flow, Reynolds number (*Re*), flow velocity (*u*), and concentrations of toluene, NO, O_2, and OH (in molecules cm^{-3}). Pressure in the drift tube P_{dt} = 1.7 Torr, pressure in the flow tube P_{ft} = 100 Torr, electric field gradient *E* = 58.8 V cm^{-1}, and *E/N* ratio = 104.4 Td.

No.	Total Flow (l min^{-1})	*Re*	*u* (m s^{-1})	[toluene] (10^{12})	[NO] (10^{11})	[O_2] (10^{14})	[OH] (10^{10})
1	28.0	2361	15.6	0.4~1.6	5.4	7.0	7.6
2	27.4	2319	15.3	0.4~1.7	5.4	7.1	1.5
3	27.8	2354	15.5	0.3~1.6	6.6	12	1.2
4	27.3	2305	15.2	0.2~1.7	6.2	13	1.0
5	27.4	2317	15.3	0.2~1.8	6.9	14	0.8
6	27.8	2353	15.6	0.2~1.8	5.8	14	0.8
7	27.5	2324	15.4	0.5~1.9	19	14	1.3

Fig. S1. Schematic diagram of the fast flow reactor coupled to an ion-drift chemical ionization mass spectrometry (ID-CIMS).

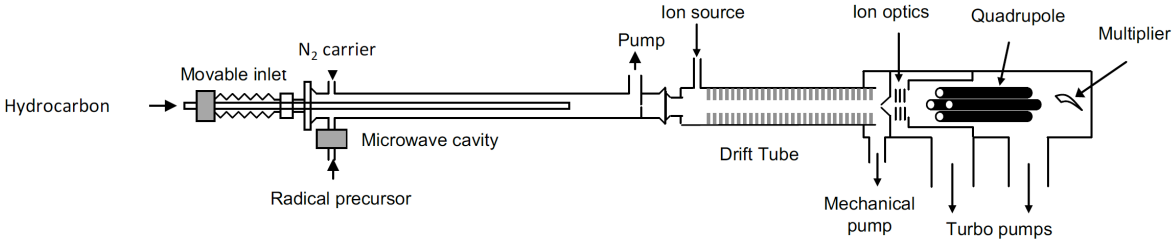


Fig. S2. Potential energy surface of the competing abstraction and addition reactions of the OH-toluene adduct with O_2.

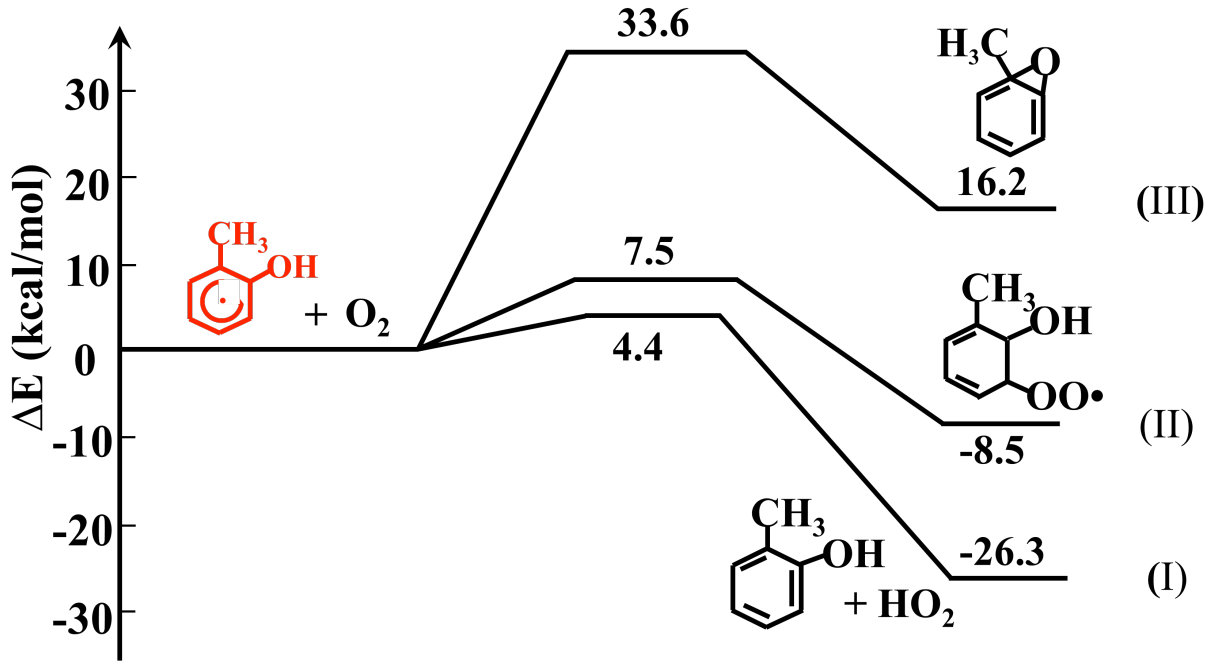


Fig. S3. Potential energy surface of the competing decomposition and cyclization for (A) o-RO_2, (B) p-RO_2, and (C) m-RO_2 (in kcal mol^{-1}).

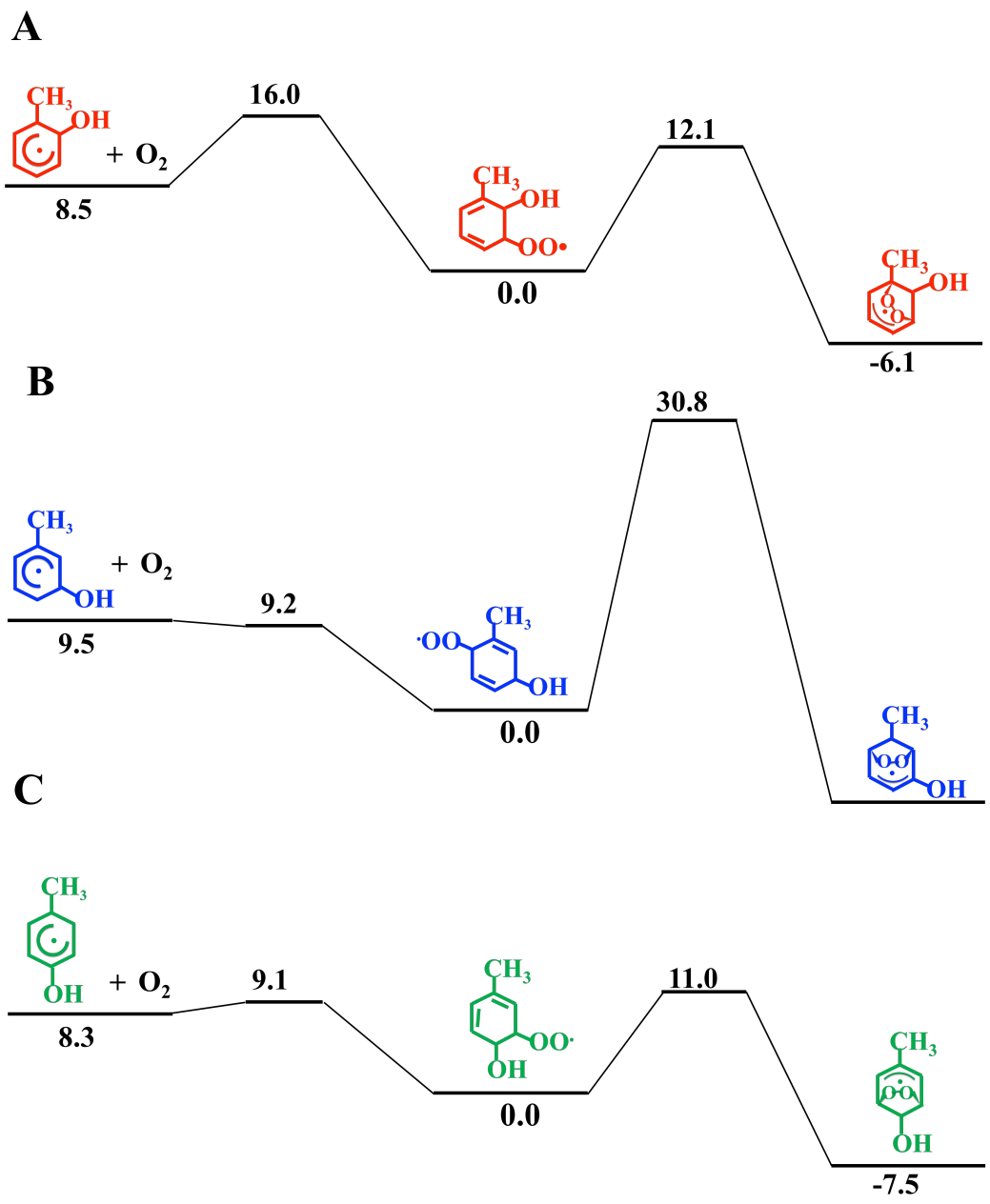


Fig. S4. Potential energy surface of the subsequent reactions of o-cresol with OH radical and O_2.

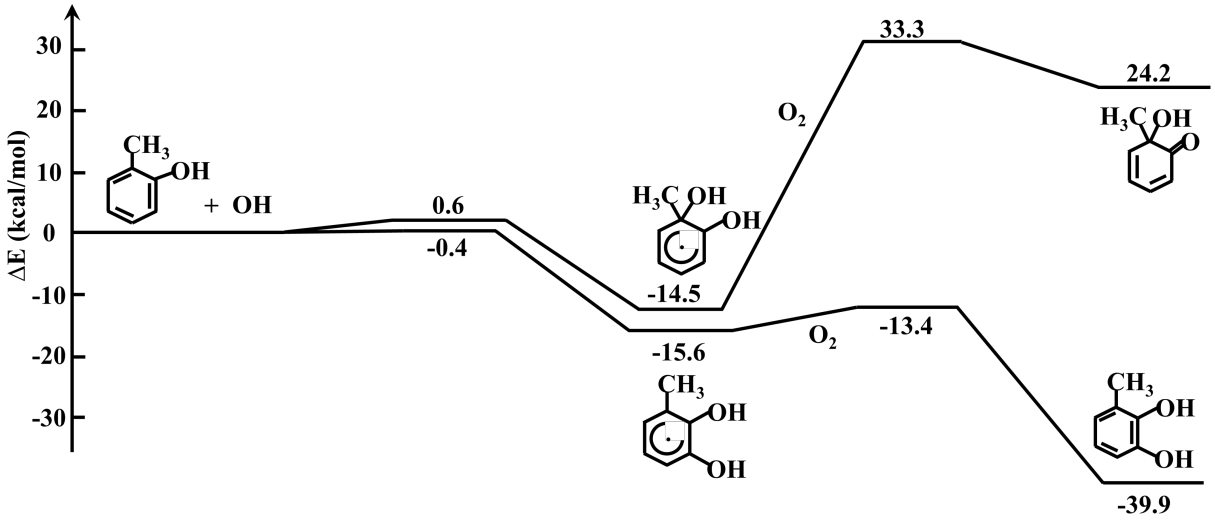
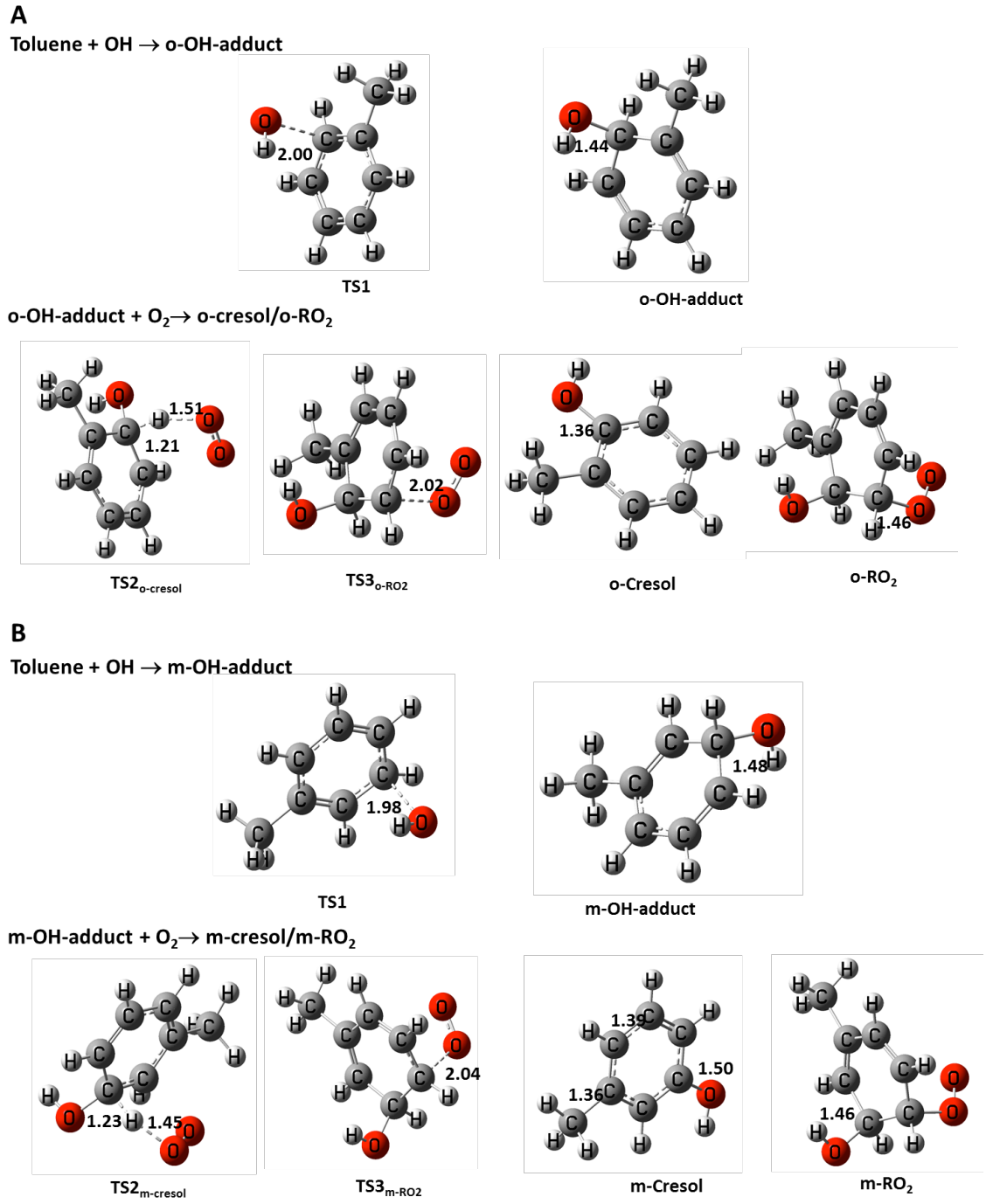
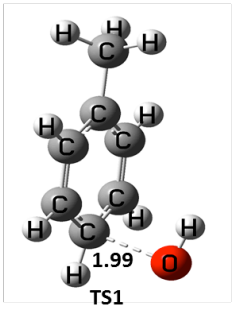


Fig. S5. Key structural parameters for the reactants, intermediates, transition states, and products involved in the OH-toluene reaction system (in Å).

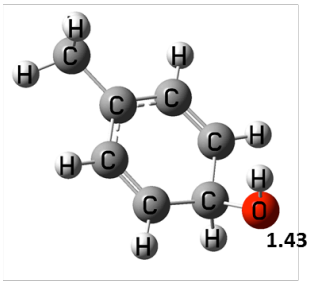


C

Toluene + OH → p-OH-adduct

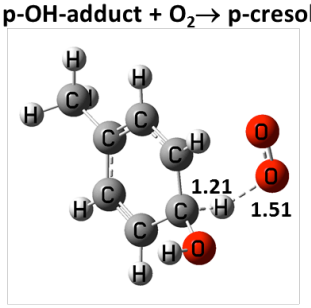


TS1

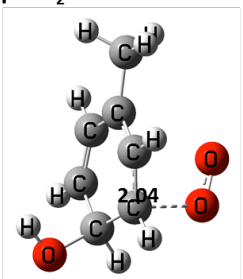


p-OH-adduct

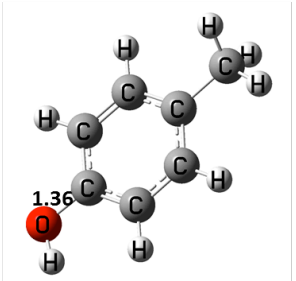
p-OH-adduct + O_2→ p-cresol/p-RO_2



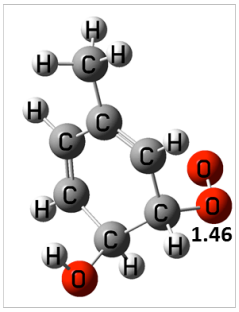
$TS1_{p\text{-}Cresol}$



$TS2_{p\text{-}RO2}$



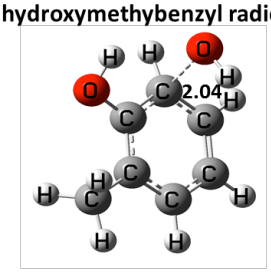
p-Cresol



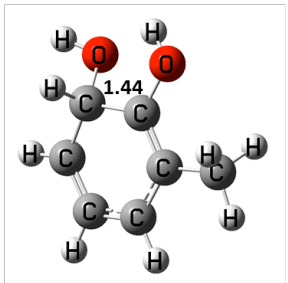
p-RO2

D

O-cresol + OH → Dihydroxymethybenzyl radical

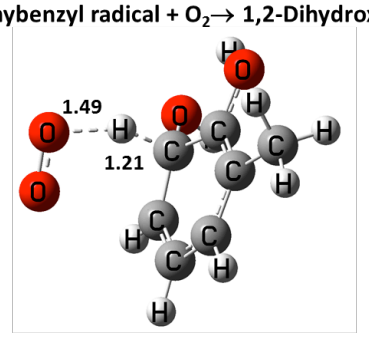


TS4

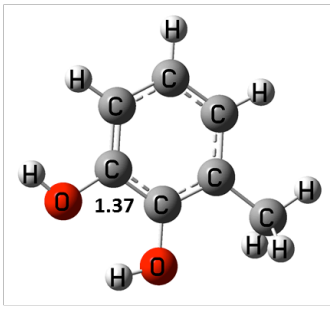


Dihydroxymethybenzyl radical

Dihydroxymethybenzyl radical + O_2→ 1,2-Dihydroxy-3-methylbenzene



TS5



1,2-Dihydroxy-3-methylbenzene